TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED / ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	
P66906US0	
US APPLICATION NO (if known, see 37 CFR 1.5)	09/926209

INTERNATIONAL APPLICATION NO	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/00456	24 February 2000	26 March 1999

TITLE OF INVENTION

OXIDATION DYEING PROCESS USING N-ACETYLCYSTEINE AS REDUCING AGENT AND A LACCASE AS OXIDIZING AGENT

APPLICANT(S) FOR DO/EO/US

Gregory PLOS

Applicant herein submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for Internatl. Preliminary Examination was made by the 19th month from earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the Internatl. Preliminary Examination report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

    International Search Report - EPO
    PCT/IB/301 Form
    PCT/IB/304 Form
    PCT/IB/308 Form
    First Page of Publication
    International Preliminary Examination Report - with no annexes

US APPLICATION NO (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
09/926209	PCT/FR00/00456	P66906US0

	CALCULATIONS	PTO USE ONLY
17. ☒ The following fees are submitted:		
Basic National Fee (37 CFR 1.492(a)(1)-(5)):		
Internatl. prelim. examination fee paid to USPTO (37 CFR 1.492 (a) (1)) . . $690.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.492 (a) (2)) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) . . $710.00		
Neither international preliminary examination fee (37 CFR 1.492 (a) (3)) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO) **$1000.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.492 (a) (4)) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00		
Search Report prepared by the EPO or JPO (37 CFR 1.492 (a) (5)) **$860.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860.00	
Surcharge of $130.00 for furnishing the **oath or declaration** later than ☐ **20** ☐ **30** months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

Claims	**Number Filed**	**Number Extra**	Rate		
Total Claims	**37** - 20 =	-17-	x $18.00	$ 306.00	
Independent Claims	**5** - 3 =	-2-	x $80.00	$ 160.00	
☐ Multiple Dependent Claim(s) (if applicable)			+ $270.00	$	
			TOTAL OF ABOVE CALCULATIONS =	$ 1326.00	
Reduction by 1/2 for filing by **small entity**, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
			SUBTOTAL =	$ 1326.00	
Processing fee of $130 for furnishing the **English translation** later than ☐ **20** ☐ **30** months from the earliest claimed priority date (37 CFR 1.492(f))				$	
			TOTAL NATIONAL FEE =	$ 1326.00	
Fee of $40.00 for recording the enclosed **assignment** (37 CFR 1.21(h)). Assignment must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31).				$ 40.00	
			TOTAL FEES ENCLOSED =	$ 1366.00	
			Amt. to be refunded:	$	
			Amt. charged:	$	

a. ☒ A check in the amount of $ 1366.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. **06-1358** in the amount of $ ____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge my account any additional fees set forth in §1.492 during the pendency of this application, or credit any overpayment to Deposit Account No. **06-1358**. A duplicate copy of this sheet is enclosed.

SEND ALL CORRESPONDENCE TO:

JACOBSON HOLMAN PLLC
400 7th Street, N.W., Suite 600
Washington, DC 20004
202-638-6666
CUSTOMER NUMBER: 00136

By Harvey B. Jacobson Jr.
Harvey B. Jacobson, Jr.
Reg. No. 20,851

JPH&S 3/95

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Bruno PLOS, Gregory — Art Group: NA

Filed: Herewith — Atty Docket: P66906US0

Serial No.: NA

For: OXIDATION DYEING PROCESS USING N-ACETYLCYSTEINE AS REDUCING AGENT AND A LACCASE AS OXIDIZING AGENT

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application, Applicant herewith respectfully requests the following amendments:

IN THE SPECIFICATION

On page 1, immediately following the title, please insert the following sentence:--This is a nationalization of PCT/FR00/00456 filed February 24, 2000 and published in French.--

IN THE CLAIMS

Please amend the claims as follows:

1. (Amended) A process of oxidation dyeing which comprises using N-acetylcysteine as a reducing agent and a laccase as an oxidizing agent in the presence of at least one oxidation dye precursor.

2. (Amended) A process for dyeing keratin fibres which comprises:

applying to the fibres a dye composition (A) comprising at least one oxidation dye precursor and N-acetylcysteine as a reducing agent in a medium which is suitable for dyeing; and

developing the color in the presence of air in an alkaline, neutral or acidic medium using at least one laccase incorporated into the composition (A) or into a composition (B), the compositions (A) and (B) being mixed together immediately before use or applied one after the other to the keratin fibres.

3. (Amended) The process according to Claim 2, wherein the composition (A) comprises N-acetylcysteine in an amount of 0.005% to 2% by weight relative to the total weight of the composition (A).

4. (Amended) The process according to Claim 3, wherein the composition (A) comprises N-acetylcysteine in an amount of 0.01%

to 0.25% by weight relative to the total weight of the composition (A).

5. (Amended) The process according to Claim 2, wherein the laccase is selected from the group consisting of plant laccases, animal laccases, fungal laccases, bacterial laccases, and recombinant laccases.

6. (Amended) The process according to Claim 2, wherein the laccase is produced by plants which carry out chlorophyll synthesis.

7. (Amended) The process according to Claim 6, wherein the laccase is extracted from an Anacardiacea plant; from a Podocarpacea plant; from Rosmarinus off.; from Solanum tuberosum; from Iris sp.; from Coffea sp.; from Daucus carrota; from Vinca minor; from Persea americana; from Catharenthus roseus; from Musa sp.; from Malus pumila; from Gingko biloba; from Monotropa hypopithys (Indian pipe); from Aesculus sp.; from Acer pseudoplatanus; from Prunus persica; and from Pistacia palaestina.

8. (Amended) The process according to Claim 5, wherein the laccase is obtained from Pyricularia orizae, Polyporus

versicolor, Rhizoctonia praticola, Rhus vernicifera, Scytalidium, Polyporus pinsitus, Myceliophthora thermophila, Rhizoctonia solani, Trametes versicolor, Fomes fomentarius, Chaetomium thermophile, Neurospora crassa, Coriolus versicol, Botrytis cinerea, Rigidoporus lignosus, Phellinus noxius, Pleurotus ostreatus, Aspergillus nidulans, Podospora anserine, Agaricus bisporus, Ganoderma lucidum, Glomerella cingulata, Lactarius piperatus, Russula delica, Heterobasidion annosum, Thelephora terrestris, Cladosporium cladosporioides, Cerrena unicolor, Coriolus hirsutus, Ceriporiopsis subvermispora, Coprinus cinereus, Paneolus papilionaceus, Panaeolus sphinctrinus, Schizophyllum commune, Dichomitius squalens, or variants thereof.

9. (Amended) The process according to Claim 2, wherein the laccase is present in amounts ranging from 0.5 to 3,000 lacu per 100 g of the composition applied to the keratin fibres.

10. (Amended) The process according to Claim 2, wherein the oxidation dye precursors of the composition (A) are selected from the group consisting of: ortho- and para-phenylenediamines; bis(phenyl)alkylenediamines; ortho- and para-aminophenols; heterocyclic bases; and addition salts thereof with an acid.

11. (Amended) The process according to Claim 10, wherein the oxidation dye precursors are present in a proportion of 0.0005% to 12% by weight relative to the total weight of the composition (A).

12. (Amended) The process according to Claim 2, wherein the couplers of the composition (A) are selected from the group consisting of meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers, and the addition salts thereof with an acid.

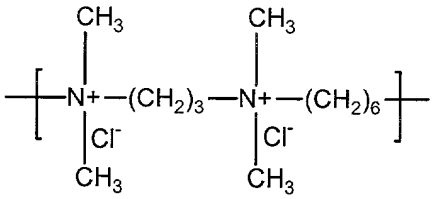
13. (Amended) The process according to Claim 12, wherein the couplers are present in a proportion of 0.0001% to 10% by weight relative to the total weight of the composition (A).

14. (Amended) The process according to Claim 10, wherein the addition salts are selected from the group consisting of hydrochlorides, hydrobromides, sulphates, tartrates, lactates, and acetates.

15. (Amended) The process according to Claim 2, wherein the composition (A), the composition (B), or a mixture thereof further comprises direct dyes.

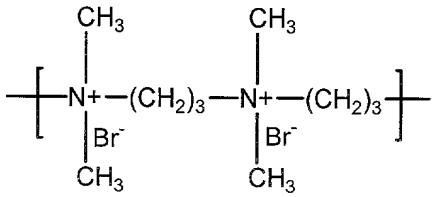
16. (Amended) The process according to Claim 2, wherein the composition (A), the composition (B), or a mixture thereof further comprises at least one cationic or amphoteric substantive polymer.

17. (Amended) The process according to Claim 16, wherein the substantive polymer is a poly(quaternary ammonium) polymer consisting of repeating units corresponding to formula (IV) below:



(IV)

18. (Amended) The process according to Claim 16, wherein the substantive polymer is a poly(quaternary ammonium) polymer consisting of repeating units corresponding to formula (V) below:



(V)

19. (Amended) The process according to Claim 2, wherein the composition (A) further comprises one or more adjuvants selected from the group consisting of sequestering agents, hair conditioners, silicones, preserving agents, opacifiers, anionic, nonionic or amphoteric surfactants, and mixtures thereof.

20. (Amended) The process according to Claim 2, wherein the pH value of the composition applied to the keratin fibres is between 3 and 11.

21. (Amended) A composition comprising at least one oxidation dye precursor and N-acetylcysteine in a medium suitable for dyeing a keratin fibre.

22. (Amended) A composition comprising a mixture of a composition (A) including at least one oxidation dye precursor and N-acetylcysteine in a medium suitable for dyeing a keratin fibre and a composition (B) including at least one laccase in an alkaline, neutral or acidic medium, wherein said composition is ready-to-use to dye a keratin fibre.

23. (Amended) A process for dyeing keratin fibres which comprises applying to the keratin fibres at least one composition according to Claim 21 containing at least one

laccase, for a period which is sufficient to develop the desired coloration.

24. (Amended) A process for dyeing keratin fibres, wherein a composition according to Claim 21 is mixed with a composition including at least one laccase in an alkaline, neutral or acidic medium prior to applying to the keratin fibres.

25. (Amended) The process according to Claim 22, wherein the composition is applied at a temperature of between 20°C and 60°C.

26. (Amended) A multi-compartment device, for dyeing keratin fibres comprising one compartment containing a composition (A) including at least one oxidation dye precursor and N-acetylcysteine, and a second compartment containing an oxidizing composition (B) including at least one laccase.

Please add the following claims:

27. (New) The process according to Claim 2, wherein the keratin fibres are human.

28. (New) The process according to Claim 2, wherein the laccase is present in amounts ranging from 1,000 to 6 x 10^7 u units per 100 g of the composition applied to the keratin fibres.

29. (New) The process according to Claim 2, wherein the laccase is present in amounts ranging from 20 to 3 x 10^6 ulac units per 100 g of the composition applied to the keratin fibres.

30. (New) The process according to Claim 2, wherein the pH value of the composition applied to the keratin fibres is between 4 and 9.

31. (New) The process according to Claim 2, wherein the pH value of the composition applied to the keratin fibres is between 6 and 8.

32. (New) A process for dyeing keratin fibres which comprises applying to the keratin fibres at least one composition according to Claim 22 for a period which is sufficient to develop the desired coloration.

33. (New) The process according to Claim 22, wherein the composition is applied at a temperature of between 35°C and 50°C.

34. (New) A kit for dyeing keratin fibres comprising the composition according to Claim 21 and an oxidizing composition including at least one laccase.

35. (New) The process according to Claim 12, wherein the addition salts are selected from the group consisting of hydrochlorides, hydrobromides, sulphates, tartrates, lactates, and acetates.

36. (New) The process according to Claim 19, wherein the hair conditioner is a silicone.

37. (New) The process according to Claim 2, wherein composition (A) further includes one or more couplers.

REMARKS

It is respectfully requested that the Examiner enter these amendments prior to examining the application on its merits.

Attached hereto is a marked-up version of the changes made and claims by the current amendment and a substitute specification is attached in clean form as well as a marked up version. The attached page is captioned "**VERSION WITH MARKINGS TO SHOW CHANGES MADE**".

Respectfully submitted,

JACOBSON HOLMAN, PLLC

Harvey B. Jacobson, Jr.
Reg. No. 20,851

Date: 25 September 2001

The Jenifer Building
400 Seventh Street, N.W.
Washington, DC 20004-2201
(202)638-6666

VERSION WITH MARKINGS TO SHOW CHANGES MADE

1. (Amended) A process of oxidation dyeing which comprises [Use of]

using N-acetylcysteine as a reducing agent and [of] a laccase as an oxidizing agent [in oxidation dyeing] in the presence of at least one oxidation dye precursor.

2. (Amended) A process [Process] for dyeing keratin fibres[, and in particular human keratin fibres such as the hair, characterized in that it consists] which comprises:

[- in] applying to the fibres a dye composition (A) [containing, in a medium which is suitable for dyeing,] comprising at least one oxidation dye precursor [and, optionally, one or more couplers] and[,] N-acetylcysteine as a reducing agent[, N-acetylcysteine, and] in a medium which is suitable for dyeing; and

[- in] developing the color [colour] in the presence of air in an alkaline, neutral or acidic medium using at least one laccase incorporated into the composition (A) or into a composition (B), the compositions (A) and (B) being mixed together immediately before use or applied one after the other to the keratin fibres.

3. (Amended) The process [Process] according to Claim 2, [in which] wherein the composition (A) [contains from] comprises N-acetylcysteine in an amount of 0.005% to 2% by weight relative to the total weight of the composition (A) [of N-acetylcysteine].

4. (Amended) The process [Process] according to Claim 3, [in which] wherein the composition (A) [contains from] comprises N-acetylcysteine in an amount of 0.01% to 0.25% by weight [of N-acetylcysteine] relative to the total weight of the composition (A).

5. (Amended) The process [Process] according to [any one of Claims 2 to 4] Claim 2, [in which] wherein the laccase is [chosen from laccases of plant origin, or animal origin, of fungal origin and of bacterial origin, or obtained by biotechnology] selected from the group consisting of plant laccases, animal laccases, fungal laccases, bacterial laccases, and recombinant laccases.

6. (Amended) The process [Process] according to [any one of Claims 2 to 5] Claim 2, [in which] wherein the laccase is [chosen from those] produced by plants which carry out chlorophyll synthesis.

7. (Amended) The process [Process] according to Claim 6, [in which] wherein the laccase is [chosen from those] extracted from an Anacardiacea [plants] plant; [or] from a Podocarpacea [plants,] plant; from Rosmarinus off.; from Solanum tuberosum; from Iris sp.; from Coffea sp.; from Daucus carrota; from Vinca minor; from Persea americana; from Catharenthus roseus; from Musa sp.; from Malus pumila; from Gingko biloba; from Monotropa hypopithys (Indian pipe)[,]; from Aesculus sp.; from Acer pseudoplatanus; from Prunus persica; and from Pistacia palaestina.

8. (Amended) The process [Process] according to Claim 5, [in which] wherein the laccase is [chosen from those] obtained from Pyricularia orizae, [from] Polyporus versicolor, [from] Rhizoctonia praticola, [from] Rhus vernicifera, [from] Scytalidium, [from] Polyporus pinsitus, [from] Myceliophthora thermophila, [from] Rhizoctonia solani, [from] Trametes versicolor, [from] Fomes fomentarius, [from] Chaetomium thermophile, [from] Neurospora crassa, [from] Coriolus versicol, [from] Botrytis cinerea, [from] Rigidoporus lignosus, [from] Phellinus noxius, [from] Pleurotus ostreatus, [from] Aspergillus nidulans, [from] Podospora anserine, [from] Agaricus bisporus, [from] Ganoderma lucidum, [from] Glomerella cingulata, [from]

Lactarius piperatus, [from] Russula delica, [from] Heterobasidion annosum, [from] Thelephora terrestris, [from] Cladosporium cladosporioides, [from] Cerrena unicolor, [from] Coriolus hirsutus, [from] Ceriporiopsis subvermispora, [from] Coprinus cinereus, [from] Paneolus papilionaceus, [from] Panaeolus sphinctrinus, [from] Schizophyllum commune, [from] Dichomitius squalens, or [and from] variants thereof.

9. (Amended) The process [Process] according to [any one of Claims 2 to 8] Claim 2, [in which] wherein the laccase is present in amounts ranging from 0.5 to [3 000] 3,000 [lacu, or from 1 000 to 6 x 10^7 u units; or from 20 to 3 x 10^6 ulac] units[,] per 100 g of [ready-to-use composition] the composition applied to the keratin fibres.

10. (Amended) The process [Process] according to [any one of Claims 2 to 9] Claim 2, [in which] wherein the oxidation dye precursors of the composition (A) are [chosen from] selected from the group consisting of: ortho- and para-phenylenediamines[,]; bis(phenyl)alkylenediamines[,]; ortho- and para-aminophenols[,]; [and] heterocyclic bases[,]; and [also] addition salts [of these compounds] thereof with an acid.

11. (Amended) The process [Process] according to Claim 10, [in which] wherein the oxidation dye precursors are present in a proportion of [from] 0.0005% to 12% by weight relative to the total weight of the composition (A).

12. (Amended) The process [Process] according to [any one of Claims] Claim 2 [to 11], [in which] wherein the couplers of the composition (A) are [chosen from] selected from the group consisting of meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers, and the addition salts [of these compounds] thereof with an acid.

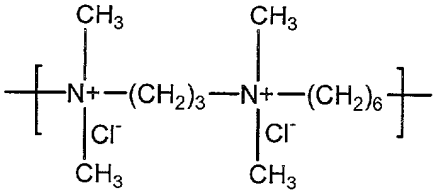
13. (Amended) The process [Process] according to Claim 12, [in which] wherein the couplers are present in a proportion of [from] 0.0001% to 10% by weight relative to the total weight of the composition (A).

14. (Amended) The process [Process] according to [Claims 10 and 12] Claim 10, [in which] wherein the addition salts [of the oxidation dye precursors and of the couplers with an acid] are [chosen from] selected from the group consisting of hydrochlorides, hydrobromides, sulphates, tartrates, lactates, and acetates.

15. (Amended) The process [Process] according to [any one of Claims 2 to 14] Claim 2, [in which] wherein the composition (A), [and/or] the composition (B), or a mixture thereof further comprises [also contains] direct dyes.

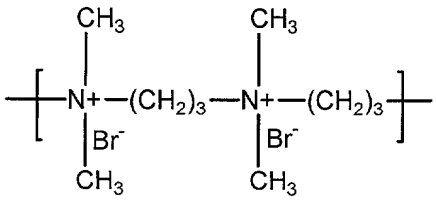
16. (Amended) The process [Process] according to [any one of Claims 2 to 15] Claim 2, [in which] wherein the composition (A), [and/or] the composition (B), or a mixture thereof further comprises [also contains] at least one cationic or amphoteric substantive polymer.

17. (Amended) The process [Process] according to Claim 16, [in which] wherein the substantive polymer is a poly(quaternary ammonium) polymer consisting of repeating units corresponding to formula (IV) below:



(IV)

18. (Amended) The process [Process] according to Claim 16, [in which] wherein the substantive polymer is a poly([quaternay]quaternary ammonium) polymer consisting of repeating units corresponding to formula (V) below:



(V)

19. (Amended) The process [Process] according to [any one of Claims 2 to 18] Claim 2, [in which] wherein the composition (A) [also contains] further comprises one or more adjuvants [chosen from] selected from the group consisting of sequestering agents, hair conditioners, [in particular] silicones, preserving agents, opacifiers, [and] anionic, nonionic or amphoteric surfactants, [or] and mixtures thereof.

20. (Amended) The process [Process] according to [any one of Claims 2 to 19] Claim 2, [in which] wherein the pH value of the [ready-to-use] composition applied to the keratin fibres is between 3 and 11[, preferably between 4 and 9 and even more preferably between 6 and 8].

21. (Amended) [Composition (A) as defined in any one of Claims 2 to 20] A composition comprising at least one oxidation dye precursor and N-acetylcysteine in a medium suitable for dyeing a keratin fibre.

22. (Amended) [Ready-to-use composition which may be obtained by mixing together the compositions (A) and (B) as defined in any one of Claims 2 to 20] A composition comprising a mixture of a composition (A) including at least one oxidation dye precursor and N-acetylcysteine in a medium suitable for dyeing a keratin fibre and a composition (B) including at least one laccase in an alkaline, neutral or acidic medium, wherein said composition is ready-to-use to dye a keratin fibre.

23. (Amended) A process [Process] for dyeing keratin fibres[, and in particular human keratin fibres such as the hair, characterized in that] which comprises applying to the keratin fibres at least one [dye] composition [(A) with laccase] according to Claim 21 containing at least one laccase, [or a ready-to-use dye composition according to Claim 22 is applied to the fibres] for a period which is sufficient to develop the desired coloration.

24. (Amended) [Process, characterized in that it comprises a preliminary step which consists in separately storing, on the one hand, the composition (A) according to Claim 21 and, on the other hand, the composition (B) according to any one of claims 2 to 20, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres] A

process for dyeing keratin fibres, wherein a composition according to Claim 21 is mixed with a composition including at least one laccase in an alkaline, neutral or acidic medium prior to applying to the keratin fibres.

25. (Amended) The process [Process] according to Claim [23] 22, [in which] wherein the [application of the ready-to-use dye] composition [is carried out] is applied at a temperature of between 20°C and 60°C [and preferably between 35°C and 50°C].

26. (Amended) A multi-compartment [Multi-compartment] device, [or "kit",] for dyeing keratin fibres[, and in particular human keratin fibres such as the hair, characterized in that it comprises] comprising [at least two compartments,] one [of which contains] compartment containing a composition (A) [containing] including at least one oxidation dye precursor [and optionally one or more couplers] and[, as a reducing agent,] N-acetylcysteine, and [another] a second compartment [contains] containing an oxidizing composition (B) [containing] including at least one laccase.

Oxidation dyeing process using N-acetylcysteine as reducing agent and a laccase as oxidizing agent

The present invention relates to a process for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, using compositions comprising, in a medium which is suitable for dyeing, at least one oxidation dye precursor, optionally, one or more couplers, and N-acetylcysteine as reducing agent, and at least one laccase as oxidizing agent.

It is known practice to dye keratin fibres, and in particular the hair, with dye compositions containing oxidation dye precursors, which are generally known as "oxidation bases" in particular ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic bases.

Oxidation dye precursors are initially colourless or only faintly coloured compounds which develop their dyeing power on the hair in the presence of an oxidizing agent. The oxidizing agent used is generally hydrogen peroxide. The formation of coloured compounds results either from a self-condensation of the "oxidation bases" or from a condensation of the "oxidation bases" with coloration modifier compounds, or "couplers", which are generally present in the dye compositions used in oxidation dyeing and which are represented more particularly by meta-phenylenediamines, meta-aminophenols and meta-diphenols and certain heterocyclic compounds.

The variety of molecules used which consist, on the one hand, of the "oxidation bases" and, on the other hand, of the "couplers", allows a wide range of colours to be obtained.

The oxidation dyeing of keratin fibres may also be achieved using oxidizing systems other than hydrogen peroxide, such as enzymatic systems. Thus, it has already been proposed in US patent 3 251 742 and patent applications FR-A-2 112 549, FR-A-2 694 018, EP-A-0 504 005, WO 95/07998, WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999 to dye keratin fibres with compositions comprising at least one oxidation dye in combination with enzymes of the laccase type, said compositions being placed in contact with atmospheric oxygen. Specifically, it has been observed that aqueous hydrogen peroxide solution can cause degradation of hair fibres and also a partial attack of the melanin of the hair, resulting in lightening of the fibre.

In order to be able to conserve the oxidation dye precursors and couplers, it is necessary to combine them with a reducing agent.

However, the Applicant has found that these reducing agents generally impede the rise of the dyes on the fibres, which is reflected by less luminous shades and less intense colorations.

In order to obtain an equivalent chromaticity, it is thus necessary to use larger amounts of dyes.

Furthermore, many reducing agents used hitherto have an inhibitory action on laccase activity.

After considerable research conducted in this matter, the Applicant has just discovered that using N-acetylcysteine as reducing agent when a laccase is used as oxidizing agent makes it possible to solve the problems mentioned above.

Specifically, it has been found that N-acetylcysteine does not inhibit laccase activity; furthermore, it has been found, surprisingly, that the mixture thus produced does not impede the rise of the oxidation dyes on the hair.

These compositions moreover give rise to more chromatic (more luminous) shades and to more intense colorations when compared with equivalent compositions containing usual reducing agents and oxidizing agents.

The colorations obtained moreover show good resistance to perspiration, light and shampooing.

The invention also makes it possible to reduce the amount of colorant active materials used in the dye compositions when compared with the conventional techniques known in the prior art.

One subject of the present invention is thus the use of N-acetylcysteine as reducing agent and of a laccase as oxidizing agent for oxidation dyeing.

Another subject of the invention relates to a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, which consists:

- in applying to the fibres a dye composition (A) containing, in a medium which is suitable for dyeing, at least one oxidation dye precursor and, optionally, one or more couplers and, as reducing agent, N-acetyl-cysteine, and

- in developing the colour in the presence of air in alkaline, neutral or acidic medium using a laccase as oxidizing agent, the laccase being incorporated into

the composition (A), in this case stored protected from air, or into a composition (B), the compositions (A) and (B) being, in this second case, mixed immediately before use or applied one after the other to the keratin fibres.

In one preferred embodiment of the invention, the N-acetylcysteine is present in proportions of from 0.005% to 2% relative to the total weight of the composition (A) and even more preferably from 0.01% to 0.25%.

The laccase(s) used in the process in accordance with the invention may be chosen in particular from laccases of plant origin, of animal origin, of fungal origin (yeasts, moulds, fungi) or of bacterial origin, the organisms of origin possibly being monocellular or multicellular. They can be obtained by biotechnology.

Among the laccases of plant origin which may be used according to the invention, mention may be made of the laccases produced by plants which carry out chlorophyll synthesis, such as those mentioned in patent application FR-A-2 694 018, for instance those found in extracts of Anacardiacea plants such as, for example, extracts of Magnifera indica, Schinus molle or Pleiogynium timoriense; in extracts of Podocarpacea plants; of Rosmarinus off.; of Solanum tuberosum; of Iris sp.; of Coffea sp.; of Daucus carrota; of Vinca minor; of Persea americana; of Catharanthus roseus; of Musa sp.; of Malus pumila; of Gingko biloba; of Monotropa hypopithys (Indian pipe); of Aesculus sp.; of Acer pseudoplatanus; of Prunus persica and of Pistacia palaestina.

Among the laccases of fungal origin, optionally obtained by biotechnology, which can be used according to the invention, mention may be made of the laccase(s) obtained

from Polyporus versicolor, from Rhizoctonia praticola and from Rhus vernicifera as described, for example, in patent applications FR-A-2 112 549 and EP-A-504 005; the laccases described in patent applications WO 95/07988, WO 95/33836, WO 95/33837, WO 96/00290, WO 97/19998 and WO 97/19999, the content of which forms an integral part of the present description, such as, for example, the laccase(s) obtained from Scytalidium, from Polyporus pinsitus, from Myceliophthora thermophila, from Rhizoctonia solani, from Pyricularia orizae, and variants thereof. Mention may also be made of the laccase(s) obtained from Trametes versicolor, from Fomes fomentarius, from Chaetomium thermophile, from Neurospora crassa, from Coriolus versicol, from Botrytis cinerea, from Rigidoporus lignosus, from Phellinus noxius, from Pleurotus ostreatus, from Aspergillus nidulans, from Podospora anserina, from Agaricus bisporus, from Ganoderma lucidum, from Glomerella cingulata, from Lactarius piperatus, from Russula delica, from Heterobasidion annosum, from Thelephora terrestris, from Cladosporium cladosporioides, from Cerrena unicolor, from Coriolus hirsutus, from Ceriporiopsis subvermispora, from Coprinus cinereus, from Panaeolus papilionaceus, from Panaeolus sphinctrinus, from Schizophyllum commune, from Dichomitius squalens, and from variants thereof.

Laccases of fungal origin, optionally obtained by biotechnology, will more preferably be chosen.

The enzymatic activity of the laccases of the invention having syringaldazine among their substrates can be defined by the oxidation of syringaldazine under aerobic conditions. One Lacu unit corresponds to the amount of enzyme which catalyses the conversion of 1 mmol of syringaldazine per minute at pH 5.5 and at 30°C. One u unit corresponds to the amount of enzyme which produces

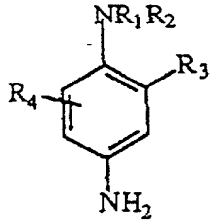
an absorbance delta of 0.001 per minute at a wavelength of 530 nm, using syringaldazine as substrate, at 30°C and at pH 6.5.

The enzymatic activity of the laccases of the invention can also be defined by the oxidation of para-phenylenediamine. One ulac unit corresponds to the amount of enzyme which produces an absorbance delta of 0.001 per minute at a wavelength of 496.5 nm, using para-phenylenediamine as substrate (64 mM), at 30°C and at pH 5.

According to the invention, it is preferred to determine the enzymatic activity in ulac units.

The amounts of laccase used in the compositions of the invention will vary as a function of the nature of the laccase chosen. Preferably, they will vary from 0.5 to 3 000 lacu, or from 1 000 to 6×10^7 u units; or from 20 to 3×10^6 ulac units, per 100 g of composition applied to the hair.

The oxidation dye precursors which may be used in the context of the present invention are chosen from those conventionally known in oxidation dyeing. Mention may be made in particular of ortho-phenylenediamines, the para-phenylenediamines of formula (I) below and the addition salts of these compounds with an acid



(I)

in which

R_1 represents a hydrogen atom or a C_{1-4} alkyl, C_{1-4} monohydroxyalkyl, C_{2-4} polyhydroxyalkyl or 4'-aminophenyl radical,

R_2 represents a hydrogen atom or a C_{1-4} alkyl, C_{1-4} monohydroxyalkyl or C_{2-4} polyhydroxyalkyl radical,

R_3 represents a hydrogen atom, a halogen atom such as a chlorine atom, or a C_{1-4} alkyl, sulpho, carboxyl, C_{1-4} monohyroxyalkyl or C_{1-4} hydroxyalkoxy radical,

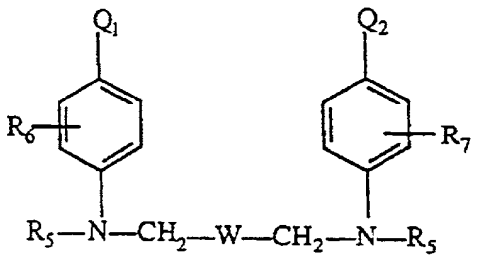
R_4 represents a hydrogen atom or a C_{1-4} alkyl radical.

Among the para-phenylenediamines of formula (I) above, mention may be made in particular of para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis(β-hydroxyethyl)-para-phenylenediamine, 4-N,N-bis(β-hydroxyethyl)amino-3-methylaniline, 4-N,N-bis(β-hydroxyethyl)amino-3-chloroaniline, 2-β-hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-(β-hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-(β-hydroxyethyl)-para-phenylenediamine, N-(β,γ-dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine and 2-β-hydroxyethyloxy-para-phenylenediamine, and the addition salts of these compounds with an acid.

Among the para-phenylenediamines of formula (I) above, the ones most particularly preferred are para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2-β-hydroxyethyl-para-phenylenediamine,

2-β-hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis(β-hydroxyethyl)-para-phenylenediamine and 2-chloro-para-phenylenediamine, and the addition salts of these compounds with an acid.

- bis(phenyl)alkylenediamines of formula (II):



(II)

in which

Q_1 and Q_2, which may be identical or different, represent a hydroxyl radical or a radical NHR_8 in which R_8 represents a hydrogen atom or a C_{1-4} alkyl radical,

R_5 represents a hydrogen atom or a C_{1-4} alkyl, C_{1-4} monohydroxyalkyl or C_{2-4} polyhydroxyalkyl radical or a C_{1-4} aminoalkyl radical in which the amino group may be substituted,

R_6 and R_7, which may be identical or different, represent a hydrogen or halogen atom or a C_{1-4} alkyl radical,

W represents a radical chosen from the group formed by the following radicals:

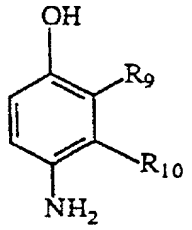
$-(CH_2)_n-$; $-(CH_2)_m-O-(CH_2)_m-$; $-(CH_2)_m-CHOH-(CH_2)_m-$ and $-(CH_2)_m-N(CH_3)-(CH_2)_m-$;

in which n is an integer between 0 and 8 inclusive and m is an integer between 0 and 4 inclusive, and the addition salts of such compounds with an acid.

Among the bis(phenyl)alkylenediamines of formula (II) above, mention may be made in particular of N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diamino-2-propanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis-(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis-(4-aminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4-amino-3-methylphenyl)ethylenediamine and the addition salts of these compounds with an acid.

Among these bis(phenyl)alkylenediamines of formula (II), N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diamino-2-propanol, or an addition salt thereof with an acid, is recommended in particular.

- the para-aminophenols corresponding to formula (III):



(III)

in which

R_9 represents a hydrogen atom or a C_{1-4} alkyl, C_{1-4} monohydroxyalkyl, (C_{1-4})alkoxy(C_{1-4})alkyl or C_{1-4} aminoalkyl, or hydroxy(C_{1-4})alkoxyamino(C_{1-4})alkyl radical;

R_{10} represents a hydrogen or fluorine atom or a C_{1-4} alkyl, C_{1-4} monohydroxyalkyl, C_{2-4} polyhydroxyalkyl, C_{1-4} aminoalkyl, cyano(C_{1-4})alkyl or (C_{1-4})alkoxy(C_{1-4})alkyl radical, and the addition salts of such compounds with an

acid,
with the proviso that at least one of the radicals R_9 and R_{10} represents a hydrogen atom.

Among the para-aminophenols of formula (III) above, mention may be made in particular of para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenyl and 4-amino-2-(β-hydroxyethylaminomethyl)phenol, and the addition salts of these compounds with an acid.

- the ortho-aminophenols which may be used as oxidation bases in the context of the present invention are chosen in particular from 2-aminophenol, 2-amino-1-hydroxy-5-methylbenzene, 2-amino-1-hydroxy-6-methylbenzene and 5-acetamido-2-aminophenol, and the addition salts of these compounds with an acid;

- the heterocyclic bases which may be used as oxidation bases in the context of the present invention are chosen in particular from pyridine derivatives, pyrimidine derivatives and pyrazole derivatives, and the addition salts of these compounds with an acid.

Among the pyridine derivatives, mention may be made more particularly of the compounds described, for example, in patents GB-1 026 978 and GB-1 153 196, such as 2,5-diaminopyridine, and the addition salts of such compounds with an acid.

Among the pyrimidine derivatives, mention may be made in particular of the compounds described, for example, in German patent DE-2 359 399 or Japanese patent JP-88-169 571, such as 2,4,5,6-tetraaminopyrimidine or

4-hydroxy-2,5,6-triaminopyrimidine, and the addition salts of such compounds with an acid.

Among the pyrazole derivatives, mention may be made more particularly of the compounds described in patents DE-3 843 892 and DE-4 133 957 and patent applications WO-94/08969 and WO-94/08970, such as 4,5-diamino-1-methylpyrazole, 3,4-diaminopyrazole and 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, and the addition salts of these compounds with an acid.

According to the invention, the oxidation dye precursor(s) preferably represent(s) from 0.0005% to 12% by weight relative to the total weight of the composition (A) and better still from 0.005% to 6% by weight approximately.

The couplers which may be used in the dyeing process according to the invention are those conventionally used in oxidation dye compositions, i.e. meta-phenylenediamines, meta-aminophenols and meta-diphenols (resorcinols), mono- or polyhydroxylated naphthalene derivatives, sesamol and its derivatives and heterocyclic compounds such as, for example, indole couplers, indoline couplers and pyridine couplers, and the addition salts of such compounds with an acid.

These couplers may be chosen in particular from 2-methyl-5-aminophenol, 5-N-(β-hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-(β-hydroxyethoxy)benzene, 2-amino-4-(β-hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis-(2,4-diaminophenoxy)propane, sesamol, α-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine,

1H-3-methylpyrazol-5-one and 1-phenyl-3-methylpyrazol-5-one, and the addition salts of such compounds with an acid.

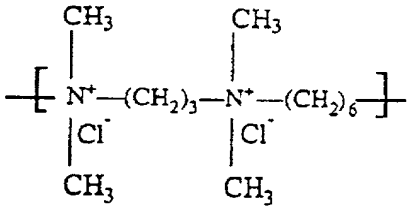
When they are present, these couplers preferably represent from about 0.0001% to 10% by weight of the total weight of the composition (A) and in particular from about 0.005% to 5% by weight.

In general, the addition salts of chromogenic compounds with an acid, i.e. oxidation bases and couplers, are chosen in particular from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

The composition (A) may contain, in addition to the oxidation dye precursors defined above and the optional combined couplers, direct dyes to enrich the shades with glints. These direct dyes may be chosen in particular from nitro dyes, azo dyes and anthraquinone dyes.

The composition (A) and/or the composition (B) may also contain at least one cationic or amphoteric substantive polymer such as those defined in EP-A-0 673 641, among which it is advantageously preferred to use:

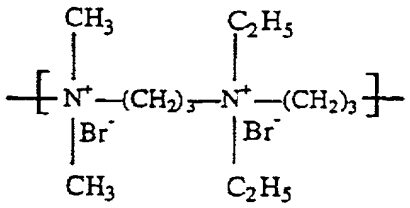
- the poly(quaternary ammonium) polymers prepared and described in French patent 2 270 846, consisting of repeating units corresponding to formula (IV) below:



(IV)

and in which the weight-average molar mass, determined by gel permeation chromatography, is between 9 500 and 9 900;

- the poly(quaternary ammonium) polymers prepared and described in French patent 2 270 846, consisting of repeating units corresponding to formula (V) below:



(V)

and in which the weight-average molar mass, determined by gel permeation chromatography, is about 1 200.

The medium for the composition (A) which is suitable for dyeing is preferably an aqueous medium consisting mainly of water and optionally containing cosmetically acceptable organic solvents, among which are alcohols such as ethyl alcohol, isopropyl alcohol, benzyl alcohol and phenylethyl alcohol; glycols or glycol ethers such as ethylene glycol monomethyl, monoethyl and monobutyl ethers, propylene glycol or its ethers such as propylene glycol monomethyl ether; butylene glycol; dipropylene glycol, and also diethylene glycol alkyl ethers such as, for example, diethylene glycol monomethyl or monobutyl ether, in concentrations of between about 0.5% and 20% by weight and preferably between about 2% and 10% by weight relative to the total weight of the composition.

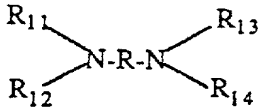
The composition (A) may also contain an effective amount of other agents commonly used in the field of oxidation dyeing. These adjuvants are, for example, sequestering

agents, hair conditioners and in particular silicones, preserving agents, opacifiers, etc., and optionally anionic, nonionic or amphoteric surfactants, or mixtures thereof.

Needless to say, a person skilled in the art will take care to select the optional additional compound(s) mentioned above, such that the advantageous properties intrinsically associated with the dye composition according to the invention are not, or are essentially not, adversely effected by the addition(s) envisaged.

The pH values for compositions (A) and (B) may be chosen in particular such that the pH value of the ready-to-use composition, resulting from mixing together the dye composition (A) and the oxidizing composition (B), is generally between 3 and 11, preferably between 4 and 9 and even more preferably between 6 and 8. They may be adjusted by means of acidifying or basifying agents that are well known in the art of oxidation dyeing of keratin fibres.

Among the basifying agents which may be mentioned, for example, are aqueous ammonia, alkali metal carbonates, alkanolamines such as monoethanolamine, diethanolamine and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and compounds of formula (VI) below:



(VI)

in which R is a propylene residue optionally substituted with a hydroxyl group or a C_{1-4} alkyl radical; R_{11}, R_{12}, R_{13}

and R_{14}, which may be identical or different, represent a hydrogen atom or a C_{1-4} alkyl or C_{1-4} hydroxyalkyl radical.

The acidifying agents are conventionally, by way of example, mineral or organic acids, such as hydrochloric acid, orthophosphoric acid, carboxylic acids such as tartaric acid, citric acid or lactic acid, or sulphonic acids.

Another subject of the present invention is a ready-to-use composition for dyeing keratin fibres, which contains laccase and the oxidation dye precursor(s), or which may be obtained by mixing together the compositions (A) and (B) defined above.

The subject of the invention is also a process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, using the dye compositions as defined above.

According to this process, at least one dye composition (A) as defined above with laccase or a ready-to-use dye composition as defined above is applied to the fibres for a period which is sufficient to develop the desired coloration, after which the fibres are rinsed, optionally washed with shampoo, rinsed again and dried. The time required to develop the coloration on the keratin fibres is generally between 3 and 60 minutes and more specifically between 5 and 40 minutes.

The application of the ready-to-use dye composition may take place in particular at a temperature of between room temperature (20°C) and 60°C and preferably between 35°C and 50°C.

According to one particular embodiment of the invention, the process comprises a preliminary step which consists in separately storing, on the one hand, a composition (A) as defined above and, on the other hand, a composition (B) defined above, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

A subject of the invention is also multi-compartment dyeing devices, or dyeing "kits" comprising at least two compartments, one of which contains a composition (A) containing at least one oxidation dye precursor and optionally one or more couplers and, as reducing agent, N-acetylcysteine, and another contains an oxidizing composition (B) containing at least one laccase. These devices may be equipped with a means for applying the desired mixture to the hair, such as the devices described in patent FR-2 586 913.

Needless to say, the preceding description has been given purely by way of illustration and with no limitation, and that variants or modifications may be made thereto in the context of the present invention.

Concrete examples illustrating the invention will now be given, without, however, being limiting in nature.

COMPARATIVE EXAMPLES

The dye compositions below are prepared (contents in grams):

EXAMPLE	1 (*)	2 (*)	3	4 (*)
para-Phenylenediamine (10^{-3} mol)	0.108 g	0.108 g	0.108 g	0.108 g
1-Methyl-2-hydroxy-4-aminobenzene (10^{-3} mol)	0.123 g	0.123 g	0.123 g	0.123 g
N-Acetyl-L-cysteine	-	-	0.1 g	-
Glucose	-	5 g	-	-
Erythorbic acid	-	-	-	0.3 g
Phosphate buffer sold under the name Titrisol by the company Merck	pH 7	pH 7	pH 7	pH 7
Demineralized water qs	(100-x) g	(100-x) g	(100-x) g	(100-x) g

(*) Examples not in accordance with the invention

At the time of use, x g of a laccase solution is added in order to obtain a final dye composition with a laccase concentration equal to 10^7 u units.

Next, each of the dye compositions obtained was applied to locks of natural grey hair containing 90% white hairs, at a rate of 5 g of composition per g of hair, for 30 minutes at 40°C. The hair was then rinsed, washed with shampoo, washed again and then dried.

The hair dyed with compositions 1*, 2* and 3 had the same shade (mid red-purple).

In order to determine the rise of the coloration more precisely, the colour of the locks was evaluated before and after dyeing in the Munsell system, using a Minolta CM-2002® colorimeter.

According to the Munsell notation, a colour is defined by the expression H V/C in which the three parameters denote, respectively, the shade or Hue (H), the intensity or Value (V) and the purity or Chromaticity (C), the oblique line in this expression simply being a convention and not representing a ratio.

The difference between the colour of the lock before dyeing and the colour of the lock after dyeing expresses the intensity of the coloration and was calculated by applying the Nickerson formula:

$$\Delta E = 0.4\ C_0\Delta H + 6\Delta V + 3\Delta C$$

as described, for example, in "Couleur, Industrie et Technique"; pages 14-17; vol. No. 5; 1978.

In this formula, ΔE represents the difference in colour between two locks, ΔH, ΔV and ΔC represent the variation in absolute value of the parameters H, V and C, and C_0 represents the purity of the lock relative to which it is desired to evaluate the colour difference.

The greater the value of ΔE, the more intense the coloration.

The results are given in the table below.

Composition	ΔE
1 (*)	30.94
2 (*)	31.29
3	32.07
4 (*)	5.75

These results show that composition 2 not in accordance with the invention and composition 3 in accordance with

the invention give a coloration which is as intense as composition 1 not in accordance with the invention and which contains no reducing agent. On the other hand, the coloration obtained with composition 4* using erythorbic acid as reducing agent is weak. Thus, the use of N-acetylcysteine does not impede the rise of the coloration, and makes it possible to obtain colorations that are as intense as those obtained without reducing agent.

The dye compositions 2* and 3 mentioned above were also stored at an ambient temperature of 22°C ± 2°C for 2 weeks.

The same colorations as those described above were then carried out.

The results are given in the table below:

Composition	ΔE
2 (*)	13.58
3	31.35

Thus, only the use of N-acetylcysteine as reducing agent makes it possible to reduce the oxidation of the dye precursors while at the same time not modifying over time the rise in coloration on the fibres.

CLAIMS

1. Use of N-acetylcysteine as reducing agent and of a laccase as oxidizing agent in oxidation dyeing in the presence of at least one oxidation dye precursor.

2. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that it consits:

   - in applying to the fibres a dye composition (A) containing, in a medium which is suitable for dyeing, at least one oxidation dye precursor and, optionally, one or more couplers and, as reducing agent, N-acetylcysteine, and

   - in developing the colour in the presence of air in alkaline, neutral or acidic medium using at least one laccase incorporated into the composition (A) or into a composition (B),

   the compositions (A) and (B) being mixed together immediately before use or applied one after the other to the keratin fibres.

3. Process according to Claim 2, in which the composition (A) contains from 0.005% to 2% by weight relative to the total weight of the composition (A) of N-acetylcysteine.

4. Process according to Claim 3, in which the composition (A) contains from 0.01% to 0.25% by weight of N-acetylcysteine relative to the total weight of the composition (A).

5. Process according to any one of Claims 2 to 4, in which the laccase is chosen from laccases of plant origin, of animal origin, of fungal origin and of bacterial origin, or obtained by biotechnology.

6. Process according to any one of Claims 2 to 5, in which the laccase is chosen from those produced by plants which carry out chlorophyll synthesis.

7. Process according to Claim 6, in which the laccase is chosen from those extracted from Anacardiacea plants or Podocarpacea plants, from Rosmarinus off.; from Solanum tuberosum; from Iris sp.; from Coffea sp.; from Daucus carrota; from Vinca minor; from Persea americana; from Catharenthus roseus; from Musa sp.; from Malus pumila; from Gingko biloba; from Monotropa hypopithys (Indian pipe), from Aesculus sp.; from Acer pseudoplatanus; from Prunus persica and from Pistacia palaestina.

8. Process according to Claim 5, in which the laccase is chosen from those obtained from Pyricularia orizae, from Polyporus versicolor, from Rhizoctonia praticola, from Rhus vernicifera, from Scytalidium, from Polyporus pinsitus, from Myceliophthora thermophila, from Rhizoctonia solani, from Trametes versicolor, from Fomes fomentarius, from Chaetomium thermophile, from Neurospora crassa, from Coriolus versicol, from Botrytis cinerea, from Rigidoporus lignosus, from Phellinus noxius, from Pleurotus ostreatus, from Aspergillus nidulans, from Podospora anserina, from Agaricus bisporus, from Ganoderma lucidum, from Glomerella cingulata, from Lactarius piperatus, from Russula delica, from Heterobasidion annosum, from Thelephora terrestris, from Cladosporium cladosporioides, from Cerrena unicolor,

from Coriolus hirsutus, from Ceriporiopsis subvermispora, from Coprinus cinereus, from Panaeolus papilionaceus, from Panaeolus sphinctrinus, from Schizophyllum commune, from Dichomitius squalens, and from variants thereof.

9. Process according to any one of Claims 2 to 8, in which the laccase is present in amounts ranging from 0.5 to 3 000 lacu, or from 1 000 to 6×10^7 u units; or from 20 to 3×10^6 ulac units, per 100 g of ready-to-use composition.

10. Process according to any one of Claims 2 to 9, in which the oxidation dye precursors of the composition (A) are chosen from ortho- and para-phenylenediamines, bis(phenyl)alkylenediamines, ortho- and para-aminophenols, and heterocyclic bases, and also addition salts of these compounds with an acid.

11. Process according to Claim 10, in which the oxidation dye precursors are present in a proportion of from 0.0005% to 12% by weight relative to the total weight of the composition (A).

12. Process according to any one of Claims 2 to 11, in which the couplers of the composition (A) are chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers, and the addition salts of these compounds with an acid.

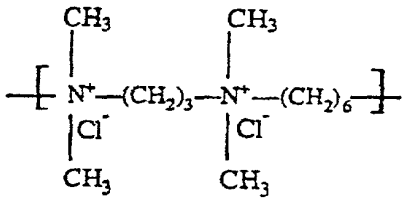
13. Process according to Claim 12, in which the couplers are present in a proportion of from 0.0001% to 10% by weight relative to the total weight of the composition (A).

14. Process according to Claims 10 and 12, in which the addition salts of the oxidation dye precursors and of the couplers with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

15. Process according to any one of Claims 2 to 14, in which the composition (A) also contains direct dyes.

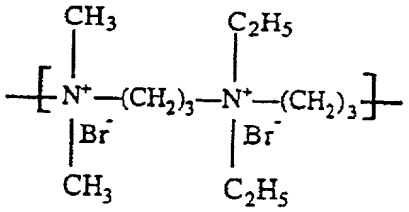
16. Process according to any one of Claims 2 to 15, in which the composition (A) and/or (B) also contains at least one cationic or amphoteric substantive polymer.

17. Process according to Claim 16, in which the substantive polymer is a poly(quaternary ammonium) polymer consisting of repeating units corresponding to formula (IV) below:



(IV)

18. Process according to Claim 16, in which the substantive polymer is a poly(quaternay ammonium) polymer consisting of repeating units corresponding to formula (V) below:



(V)

19. Process according to any one of Claims 2 to 18, in which the composition (A) also contains one or more adjuvants chosen from sequestering agents, hair conditioners, in particular silicones, preserving agents, opacifiers and anionic, nonionic or amphoteric surfactants, or mixtures thereof.

20. Process according to any one of Claims 2 to 19, in which the pH value of the ready-to-use composition is between 3 and 11, preferably between 4 and 9 and even more preferably between 6 and 8.

21. Composition (A) as defined in any one of Claims 2 to 20.

22. Ready-to-use composition which may be obtained by mixing together the compositions (A) and (B) as defined in any one of Claims 2 to 20.

23. Process for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that at least one dye composition (A) with laccase according to Claim 21 or a ready-to-use dye composition according to Claim 22 is applied to the fibres for a period which is sufficient to develop the desired coloration.

24. Process, characterized in that it comprises a preliminary step which consists in separately

storing, on the one hand, the composition (A) according to Claim 21 and, on the other hand, the composition (B) according to any one of Claims 2 to 20, and then in mixing them together at the time of use, after which this mixture is applied to the keratin fibres.

25. Process according to Claim 23, in which the application of the ready-to-use dye composition is carried out at a temperature of between 20°C and 60°C and preferably between 35°C and 50°C.

26. Multi-compartment device, or "kit", for dyeing keratin fibres, and in particular human keratin fibres such as the hair, characterized in that it comprises at least two compartments, one of which contains a composition (A) containing at least one oxidation dye precursor and optionally one or more couplers and, as reducing agent, N-acetylcysteine, and another compartment contains an oxidizing composition (B) containing at least one laccase.

DECLARATION AND POWER OF ATTORNEY U.S.A.

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ATTORNEYS' DOCKET NO.

ALL PATENTS, INCLUDING DESIGN
FOR APPLICATION BASED ON PCT, PARIS CONVENTION,
NON PRIORITY, OR PROVISIONAL APPLICATIONS

101 / 102

As a below named inventor, I declare that my residence, post office address and citizenship are stated below next to my name, the information given herein is true, that I believe that I am the original, first and sole inventor (if only one name is listed at 201 below), or an original, first and joint inventor (if plural inventors are named below at 201-203, or on additional sheets attached hereto) of the subject matter which is claimed and for which patent is sought on the invention entitled. "OXIDATION DYEING PROCESS USING N-ACETYLCYSTEINE AS REDUCING AGENT AND A LACCASE AS OXIDIZING AGENT"

which is described and claimed in ☒ PCT International Application No. PCT/FR00/00456 filed 24 February 2000

☐ the attached specification ☐ the specification in application Serial No. _____ filed _____

(if applicable) and amended on _____

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.
I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.
I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

103 / 104

Prior Foreign Application(s) (Number)	(Country)	(Day/Month/Year Filed)	Priority Claimed Yes	No
9903829	FRANCE	26 MARCH 1999	☒	☐
			☐	☐
			☐	☐

I hereby claim the benefit under Title 35, United States Cod, §119(e) of any United States provisional appplication(s) listed below:
Application No _____ Filing Date _____ Application No. _____ Filing Date _____

105

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

(Application Serial No.)	(Filing Date)	(Status: patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorneys (Registration No.) to prosecute this application, receive and act on instructions from my agent, and transact all business in the Patent and Trademark Office connected therewith. HARVEY B. JACOBSON, JR. (20,851); D. DOUGLAS PRICE (24,514); JOHN CLARKE HOLMAN (22,769); MARVIN R. STERN (20,640); MICHAEL R. SLOBASKY (26,421); JONATHAN L. SCHERER (29, 851); IRWIN M. AISENBERG (19,007); WILLIAM E. PLAYER (31,409)

SEND CORRESPONDENCE TO:	DIRECT TELEPHONE CALLS TO: (please use Attorney's Docket No.) (202) 638-6666
JACOBSON, PRICE, HOLMAN & STERN PROFESSIONAL LIMITED LIABILITY COMPANY 400 Seventh Street, N.W. Washington, D.C. 20004	JACOBSON, PRICE, HOLMAN & STERN PROFESSIONAL LIMITED LIABILITY COMPANY

*Inventor(s) name must include at least one unabbreviated first or middle name.

201	FULL NAME* OF INVENTOR	FAMILY NAME PLOS	GIVEN NAME Grégroy		MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY PARIS	STATE OR FOREIGN COUNTRY FRANCE		COUNTRY OF CITIZENSHIP FR	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS 3 rue Sextius Michel	CITY PARIS	STATE OR COUNTRY FRANCE		ZIP CODE 75015
202	FULL NAME* OF INVENTOR	FAMILY NAME	GIVEN NAME		MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY		COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY		ZIP CODE
203	FULL NAME* OF INVENTOR	FAMILY NAME	GIVEN NAME		MIDDLE NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY		COUNTRY OF CITIZENSHIP	
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I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201*	SIGNATURE OF INVENTOR 202*	SIGNATURE OF INVENTOR 203*
Gregory Plos		
DATE June 20, 2001	DATE	DATE

☐ Additional inventors are named on separately numbered sheets attached hereto.